

SYNGAS PRODUCTION FOR GAS-TO-LIQUIDS APPLICATIONS: TECHNOLOGIES, ISSUES AND OUTLOOK

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Introduction

Fischer Tropsch (F-T) chemistry understandably is often regarded as the key technological component of schemes for converting synthesis gas (or "syngas") to transportation fuels and other liquid products. However, syngas production itself accounts for more than half the capital investment and a disproportionate share of the operating costs for a gas-to-liquids (GTL) complex. A study completed earlier in 1998 by SFA Pacific examines the full range of commercial and developmental synthesis gas production technologies and provides an independent assessment of syngas production options and costs for GTL applications [1].

The manner in which syngas is produced can be influenced by, and in turn can profoundly impact, many facets of the overall GTL process design, such as:

- Plant size and location
- The need for an oxygen plant or oxygen enrichment facilities
- The physical size of downstream gas-handling equipment
- Syngas composition and its associated effects on F-T chemistry and yields
- Heat integration and gas recycle options
- Gas compression requirements
- The scope and configuration of power generation alternatives

This paper examines the status of commercial and developmental syngas production technologies in the context of GTL production based on F-T synthesis. The scope of this examination includes:

- A brief review of relevant commercial experience to date
- Consideration of the direct and indirect impacts of syngas production on GTL costs
- An update on new syngas generation technologies now under development
- Comments on the relative merits of air-blown and oxygen-blown syngas generation
- The outlook for reduced GTL capital and operating costs due to improved syngas generation

Syngas Generation Technologies

In principle, synthesis gas may be generated from any hydrocarbon feedstock. This is reflected in industrial practice, which includes large-scale syngas production from a wide variety of materials that includes natural gas, naphtha, residual oil, petroleum coke and coal. However, in the context of GTL applications, natural gas -- more specifically, low-value natural gas -- is the predominant, if not the only, feedstock of interest.

In large part, this is a reflection of the high investment costs of GTL processes which, in the absence of special circumstances, require a low or, even better, negative value feedstock to achieve attractive overall economics. Low quality residual oil or coke can, of course, have a low or even negative value. However, conversion of such feedstocks -- via gasification -- entails greater capital investment, in part due to the costs associated with materials handling, soot removal and syngas cooling and purification. The focus for GTL has thus been on associated gas, so-called stranded or remotely-located gas reserves, and larger gas reserves that are not currently being economically exploited. In the near-term, associated gas may offer the greatest potential, particularly where such gas is subject to flaring constraints and associated reinjection costs.

Chemicals from Coal: The Acetyl Value Stream

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Abstract

Well-established technologies for the conversion of syn-gas can be utilized to manufacture each of the primary materials that constitute the acetyl value chain, i.e., methanol, acetic acid (acetic anhydride) and vinyl acetate. Interest in driving the utilization of syn-gas resources further down the acetyl value chain arises not only from the necessity to efficiently utilize domestic carbon sources but also from issues of global competitiveness. The first-discovered commercializable low-water containing homogeneous catalyst system for the production of acetic acid utilizes a non-noble metal catalyst (nickel). A number of studies, including our own, have indicated that phosphines are important not only to stabilize the catalyst but they also have a substantial effect on the rate of carbonylation. We will discuss a study of this catalyst system that is based upon both kinetic and in-situ monitoring results.

Introduction

Eastman Chemical Company has demonstrated a long-term commitment to the utilization of syngas in the commercial manufacture of acetyl chemicals. Our "Chemicals from Coal" complex practices the carbonylation of methyl acetate to acetic anhydride, a

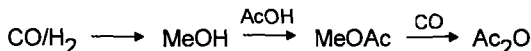


Figure 1: Eastman's Chemicals from Coal Stream

process utilizing only syngas derived feedstocks. In this facility the synthesis of acetic acid is accomplished by the methanolysis of acetic anhydride. Typically, however, the large-scale production of acetic acid is carried out by the homogeneously catalyzed low-pressure carbonylation of methanol. Commercial facilities currently utilize either a rhodium or iridium based homogeneous catalyst and a methyl iodide promoter. Early attempts to utilize less-expensive nickel catalysts indicated that severe process conditions (pressures as high as 26.7 kPa and temperatures in the range of 250-300°C) were required to achieve reasonable reaction rates. More recently, it was found that the severity of the required process conditions could be considerably reduced by the use of appropriate promoters and the nickel-catalyzed reaction became a viable competitor to other commercial catalyst systems.

The catalyst system for the nickel-catalyzed acetic acid process consists of nickel and molybdenum compounds, an iodide promoter and a phosphine. Under reaction conditions the phosphine exists largely as the phosphonium iodide (adduct with methyl iodide). However, high-pressure infrared studies suggest that substantial quantities of the free phosphine are present and available to act as ligands in the catalytically active metal complex. This is consistent with the notion that the phosphorous component of the catalyst mixture is important in suppressing the formation of the inactive $\text{Ni}(\text{CO})_4$ which is present only in trace amounts when the steady-state catalysis is rapid. It also provides an ability to modify the behavior of the catalytic process as changes in the electronic and steric properties of the phosphine are reflected in both the amount of free phosphine present under catalytic conditions and in the nature of the catalytically active species. Indeed, we have been able to observe changes in the rate of catalysis as the nature of the phosphorus promoter changes.

Experimental

The reaction systems described here have been studied by an in situ CIR-FTIR reactor. This equipment and the experimental conditions have been described.¹ Measurement of the rate of various reactions was obtained by monitoring the number of moles of carbon monoxide consumed by the reaction mixture. This was accomplished by either the use of mass-flow control meters or by monitoring the pressure-drop in a surge tank used to supply carbon monoxide to the reaction vessel. In a typical experiment NiI_2 (1.72g), PPh_3 (5.76g), $\text{Mo}(\text{CO})_6$ (0.89g), methyl iodide (25.8g), acetic acid (53.5 mL), methanol (53 mL), water (7.3mL) and methyl acetate (11 mL) were loaded into a 300 mL stirred

Results and Discussion

A mechanistic scheme that explains the major features of the reaction and is consistent with both the kinetic and in situ CIR-FTIR observations² is shown in Figure 2. It suggests that a catalytically active nickel(0) species is available as a result of both a hydrogen enabled reduction from Ni(II) and the delivery of free phosphine ligand from the equilibrium dissociation of the phosphonium salt. The catalytic cycle itself is fairly unremarkable when compared with similar postulated mechanisms for the rhodium catalysts. Methyl iodide is delivered to the catalytic carrier and an oxidative addition results in the formation of a Ni(II) alkyl iodide complex. The addition of carbon monoxide is followed by an alkyl migration and a subsequent reductive elimination allows the recovery of acetic acid product and regeneration of the carrier.

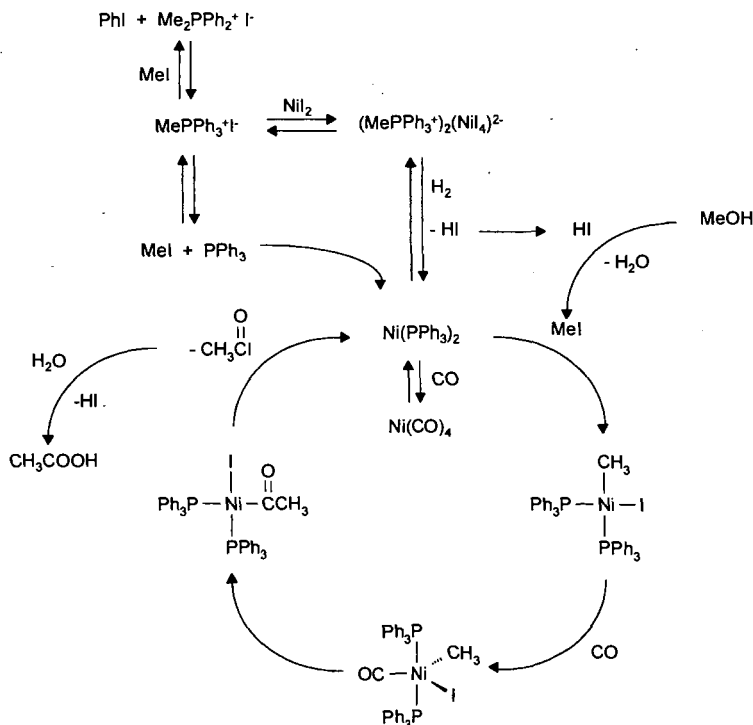


Figure 2: Mechanism of the Nickel Catalyzed Carbonylation of Methanol

CIR-FTIR observations indicate that there is no build-up of nickel carbonyl species during the course of the reaction so that the slow step(s) of the process must occur before the addition of carbon monoxide.

The course of a typical batch reaction, as measured by the uptake of carbon monoxide (Figure 3), can be used to examine catalyst activation. In this particular case one can note a persistent induction period that spans about 40 minutes followed by a period of well-behaved steady-state catalysis and finally the loss of rate associated with depletion of the reactants.

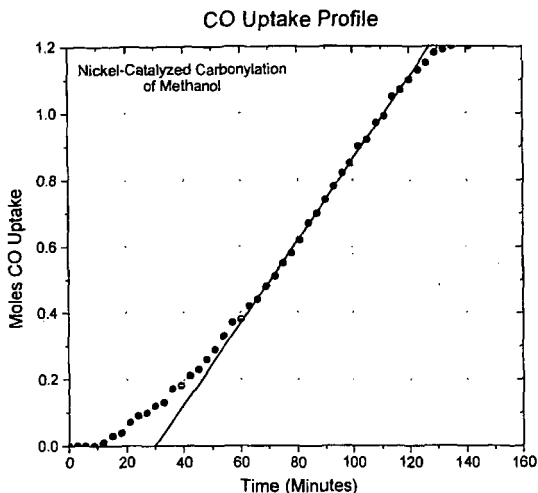


Figure 3: Course of Typical Batch Reaction

The length of the induction period has been shown to depend upon both the nature of the nickel compound charged to the reactor as well as the partial pressure of hydrogen present in it. With NiI_2 , triphenylphosphine and the reaction conditions as indicated in the experimental section the induction period is minimized. However, the details of the reduction process have not yet been elucidated and we cannot distinguish between the direct formation of " NiI_2 " or the intermediate formation of $\text{Ni}(\text{CO})_4$ which subsequently reacts with free ligand.

The rate of the reaction shows first-order dependence upon the concentration of nickel and methyl iodide. The reaction is also first-order with respect to carbon monoxide at lower pressures. These results are consistent with the CIR-FTIR observations noted above. However, at higher carbon monoxide pressures the rate of reaction is inhibited indicating that it is possible for carbon monoxide to compete effectively with the free ligand present in solution. In fact, as one might predict from this mechanism, higher concentrations of phosphine promoter are required in order to obtain the maximum rate of reaction at higher carbon monoxide partial pressures.

Also consistent with the above mechanism is the observation that the rate of catalysis depends upon the identity of the phosphine promoter used. The identity of the phosphine determines the position of the dissociative equilibrium from the phosphonium iodide and thus the amount of free ligand available as well as the rate of the reaction of the various ligand substituted nickel intermediates. It was shown that both the steric and electronic properties of the phosphine promoters play a role in determining reaction rates.

Conclusions

The mechanism of the phosphine promoted nickel-catalyzed carbonylation of methanol has been shown to involve the equilibrium dissociation of free phosphine from the phosphonium iodide present under reaction conditions. This free phosphine is able to compete effectively as ligand with carbon monoxide in the formation of the catalytically active zero-valent nickel intermediates. The rate of reaction can be favorably influenced by the nature of the phosphine promoter used and under conditions which provide rapid rates for carbonylation $\text{Ni}(\text{CO})_4$ is present in only trace quantities.

Acknowledgements

The CIR-FTIR results and rate measurements in the CIR-REACTOR were obtained at Worcester Polytechnic Institute by Professor William R. Moser and Barbara J. Marshik-Guerts.

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FISCHER TROPSCH: A FUTURISTIC VIEW

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INTRODUCTION

During the last couple of years there has been a renewed interest in the use of Fischer-Tropsch technology for the conversion of natural gas to liquids. Some of the factors that contributed to this are:

- (i) An increase in the known reserves of natural gas.
- (ii) The need to monetize remote or stranded natural gas.
- (iii) Environmental pressure to minimize the flaring of associated gas.
- (iv) Improvements in the cost-effectiveness of Fischer-Tropsch technology resulting from the development of more active catalysts and improved reactor designs.

The process to convert natural gas to liquids can be divided into three process steps:

- (i) Syngas generation
- (ii) Syngas conversion
- (iii) Hydroprocessing

Although all three of these technologies are well established, individually optimized and commercially proven, the combined use is not widely applied. This poses an interesting challenge to the designer, namely to obtain the most cost-effective combination of these three technologies. In order to make the Gas-to-Liquids (GTL) technology more competitive, the challenge goes beyond the optimization that deals only with the known aspects of these technologies. It also includes those aspects that are not commercialized yet and that may still be in the very early stages of development.

OPTIMIZATION OF EXISTING TECHNOLOGIES

SYNGAS GENERATION

To convert natural gas (mostly methane) to syngas (a mixture of H_2 and CO), the designer can choose from the following four well established reforming technologies:

- (i) Steam reforming
- (ii) Partial oxidation (POX)
- (iii) Autothermal reforming
- (iv) Combined or two-step reforming

The choice of reformer technology will have an influence on the thermal efficiency of the plant as a whole and on the capital costs of the reformer, oxygen plant (where applicable) and the Fischer-Tropsch section. One of the biggest challenges is to optimize the energy integration between the syngas generation and syngas conversion sections.

STEAM REFORMING

An obvious advantage of steam reforming is that it does not need an oxygen plant. However, since steam reformers are more costly than either POX or autothermal reformers, there is a minimum plant size above which the economy of scale of a

cryogenic oxygen plant in combination with a POX or autothermal reformer is cheaper than a steam reformer on its own.

Other disadvantages of steam reforming are:

- (i) Syngas with a H_2/CO ratio (>4) which is much higher than what is optimally needed by the Fischer-Tropsch section.
- (ii) Lower methane conversion due to a maximum operating temperature of below $900^\circ C$.
- (iii) The high usage rate of water makes it unsuitable for arid regions.

Recycling of CO_2 and removal of the excess H_2 by means of membranes can lower the H_2/CO ratio to a level acceptable to the Fischer-Tropsch reaction. Since the methane conversion is also a function of the operating pressure, decreasing the operating pressure of the reformer can increase the methane conversion. Due to the costs involved with these steps, it is most likely that steam reforming will only be considered when one or more of the following conditions hold:

- (i) A relative small GTL plant with a capacity of well below 10 000 bpd.
- (ii) The additional H_2 can be used for other applications like methanol or ammonia production.
- (iii) The natural gas has a high CO_2 content.
- (iv) Suitable water can be obtained at a low cost.

PARTIAL OXIDATION REFORMING

The non-catalytic partial combustion of methane produces syngas with a H_2/CO ratio (<2) close to the optimum needed by the Fischer-Tropsch section. This low H_2/CO ratio gas results from the very little, if any, steam that is used in the process. Due to the absence of catalyst, the reformer operates at an exit temperature of about $1400^\circ C$. This high temperature and the absence of catalyst have the following disadvantages as compared to an autothermal reformer:

- (i) Formation of soot and much higher levels of ammonia and HCN, which necessitates the use of a scrubber to clean the gas.
- (ii) Higher oxygen consumption.
- (iii) Due to the absence of the water-gas shift reaction, the unconverted methane as well as the methane produced by the Fischer-Tropsch reaction can not be recycled to the reformer without removing the CO_2 from the Fischer-Tropsch tail gas.

Depending on the energy needs of the plant, the syngas from the reformer can either be cooled by means of a water quench or by the production of steam in a heat exchanger. A quench system is the less costly of the two, but is also less thermally efficient. In designing a POX based GTL plant, the choice between a quench or a waste heat reboiler will depend on the relative cost of capital and energy.

AUTOTHERMAL REFORMING

Unlike partial oxidation reforming, autothermal reforming uses a catalyst to reform the natural gas to syngas in the presence of steam and oxygen. Due to the milder operating conditions (exit temperature of $\pm 1\ 000^\circ C$) and the use of steam (S/C ratio normally more than 1,3), the syngas is soot free and less ammonia and HCN are produced as compared to a POX. However, at a S/C ratio of 1,3 the syngas will have a H_2/CO ratio of about 2,5, which is higher than the ratio needed by the Fischer-Tropsch section. The H_2/CO ratio can be controlled by a combination of lowering the S/C ratio and recycling the CO_2 to the reformer. Although S/C ratios below 1,3 are not commercially used, Haldor Topsøe and Sasol have successfully completed low S/C ratio tests on a commercial scale at Sasol's synfuels plant in South Africa.

Some of the other design parameters of the syngas section that influence the cost and thermal efficiency of the GTL plant are:

- (i) The preheat temperatures of oxygen and natural gas. The higher these temperatures are, the less oxygen will be used. The maximum preheat temperatures are determined by safety factors and by the need to prevent soot formation.

- (ii) The pressure of the steam generated in the waste heat reboiler. The higher the steam-pressure, the more efficient energy can be recovered from the steam, but the more costly the steam and boiler feed water treatment systems become. The optimum steam pressure will be determined by the relative cost of capital and energy.

COMBINED REFORMING

By combining a steam reformer with an autothermal reformer, better energy utilization can be obtained than with either steam or autothermal reforming alone. Depending on the degree of energy integration and the specific operating conditions, the thermal efficiency of the GTL plant can be improved by about 1 to 2 percentage points. Although less expensive than steam reforming on its own, this type of reforming is more expensive than autothermal reforming and the choice between combined and autothermal reforming will depend on the cost of the natural gas.

SYNGAS CONVERSION

Due to its high activity and long life, cobalt-based Fischer-Tropsch catalyst is currently the catalyst of choice for the conversion of syngas to liquid fuels. The exothermic nature of the Fischer-Tropsch reaction combined with the high activity of the Co catalyst makes the removal of heat from the reactor of critical importance. In the case of a tubular fixed bed reactor, this becomes even more problematic due to the inherent temperature profiles inside the tube. This problem can be controlled by finding the balance between the tube diameter and the usage of a "quench" medium such as the recycle of inerts.

Due to the good mixing and heat transfer characteristics of a slurry phase reactor, the temperature control in such a reactor is much less of a problem than in a tubular fixed bed reactor. Care must however be taken in the design of such a reactor that, during normal operating conditions and also during the shutdown of the reactor, no stagnant zones with poor mixing occur which may result in localized hot spots. If the catalyst is exposed to too high a temperature, carbon will be formed, which may damage the structural integrity of the catalyst.

Another critical design aspect of a slurry phase reactor is the separation of the catalyst from the wax. Sasol was successful in the development of a very efficient catalyst/wax separation system. By matching the characteristics of the catalyst with those of the separation system, the loss of catalyst can be restricted to a few ppm of catalyst in the wax produced by the Fischer-Tropsch process.

Since the H_2/CO ratio of the syngas is an important design variable to maximize the production of high quality diesel, the designs of the reformer and the Fischer-Tropsch sections can not be done in isolation. The most cost effective design for both units can only be obtained by taking the mutual interaction between these units into account.

HYDROPROCESSING

The wax and hydrocarbon condensate produced by the Fischer-Tropsch process is predominantly linear paraffins with a small fraction of olefins and oxygenates. The hydrogenation of the olefins and oxygenates and the hydrocracking of the wax to naphtha and diesel can be done at relatively mild conditions.

In the design of the hydrocracker, a balance must be found between the per-pass conversion, diesel selectivity and diesel properties. The higher the per-pass conversion, the smaller the cracker will be due to the lesser recycle of material back to the cracker. This will however be at the expense of the diesel selectivity, since over cracking of the liquid to gasses will occur. Another complicating factor is that the per-pass conversion also influences the diesel quality. The higher the per-pass conversion, the better the cold flow properties but the lower the cetane value will be, due to the increased degree of isomerisation.

CAPITAL AND OPERATING COSTS

CAPITAL COST

Studies done by Sasol indicated that the total installed cost of a two train 30 000 barrel per day GTL plant is in the order of about \$24 000 per daily barrel. It is also believed that the capital cost can be further decreased to about \$20 000 per daily barrel by:

- (i) The economy of scale of larger single train capacity plants.
- (ii) The economy of scale of adding trains.
- (iii) Improved process integration and optimization.
- (iv) Progressing up the learning curve.

The capital cost associated with the syngas generation section is more than 50% of the total IBL cost of the plant.

OPERATING COST

Based on a gas cost of \$0,5 per MM BTU, the estimated operating cost is in the order of about \$10 per barrel of which the gas cost is \$5 per barrel. The main areas of energy loss from the process are the syngas generation and syngas conversion sections. The oxygen plant and reformer combination is responsible for about 45% and the Fischer-Tropsch section for about 50% of the energy losses from the plant.

About 50% of energy loss from the Fischer-Tropsch plant is due to condensing of the reaction water produced by the Fischer-Tropsch reaction and the balance results from the inefficiency with which energy is recovered from the relatively low pressure steam.

FUTURE IMPROVEMENTS

In order to have the greatest impact on the economics of the process, future breakthroughs should be in areas that decrease the capitals cost of syngas generation and/or improve the thermal efficiency of the plant as a whole.

An obvious way of improving the thermal efficiency of the process is to combine it with a power generation plant. Such a combination will create a more efficient utilization of the low pressure steam produced by the Fischer-Tropsch process. If the energy associated with this steam is sold at the same price as that of the natural gas (\$0,5 per MM BTU), an additional income of about \$0,5 per barrel can be obtained.

Some of the changes to the reforming section that can increase the thermal efficiency of the process are:

- (i) The use of a heat exchange reformer in combination with an autothermal reformer.
- (ii) The use of a feed/product heat exchanger to recover energy from the reformer outlet.

HEAT EXCHANGE REFORMING

The combination of a heat exchange reformer with an autothermal reformer is very similar to combined reforming, the major difference being that the energy to the steam reformer is not supplied by a fired heater but by the exit gas from the autothermal reformer.

The potential benefits of such a reforming configuration are:

- (i) Savings of about 30% in oxygen consumption.
- (ii) An increase of about 4 percentage points in the thermal efficiency of the plant.

One of the technical issues that must be solved is the potential problem of metal dusting in the heat exchange reformer.

FEED/PRODUCT HEAT EXCHANGE

The oxygen consumption can be decreased by about 3,5% and the production of liquid fuels can be increased by about 2,5% if a feed/product heat exchanger is used to

preheat the natural gas to the reformer. As in the case of heat exchange reforming, metal dusting is also one of the major technical problems that would have to be solved.

OXYGEN TRANSFER MEMBRANES

Another way of eliminating the oxygen plant is to use ceramic membranes to separate the oxygen from the air. In addition to the capital cost savings associated with the elimination of an oxygen plant, the thermal efficiency of the plant can also be improved by combining the oxygen removal and reforming sections into one unit. Early indications are that this technology should significantly reduce the capital cost of the syngas generation section of the GTL plant.

Some of the technical issues that are being researched include the maximization of the oxygen flux and the mechanical strength of the ceramic tubes.

OTHER POTENTIAL IMPROVEMENTS

The Co catalyst can be improved by:

- (i) Increasing the catalyst life by making it more resistant to irreversible sulphur poisoning.
- (ii) Changing the selectivity dependency on the H_2/CO ratio to such an extent that high diesel yields can be obtained at H_2/CO ratios similar to the usage ratio. The advantage of such a catalyst would be that, due to the increase in reaction rate at higher H_2/CO ratios, much less catalyst would be needed for the same conversion. To obtain the same conversions at H_2/CO ratio's of 2 and 1,6, 50% more catalyst is needed at the lower H_2/CO ratio.

CONCLUSIONS

Although the three main processing steps of a GTL plant have been individually optimized for other applications, opportunities do exist to decrease the capital and operating costs by re-optimizing these processing steps for GTL applications. In addition to these optimization opportunities, there are other potential breakthroughs that can also significantly reduce the operating and capital costs of a GTL plant.

Fischer-Tropsch Synthesis: Current Mechanism and Futuristic Needs

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KEYWORDS: Fischer-Tropsch Synthesis; reaction mechanism; isotopic tracer studies

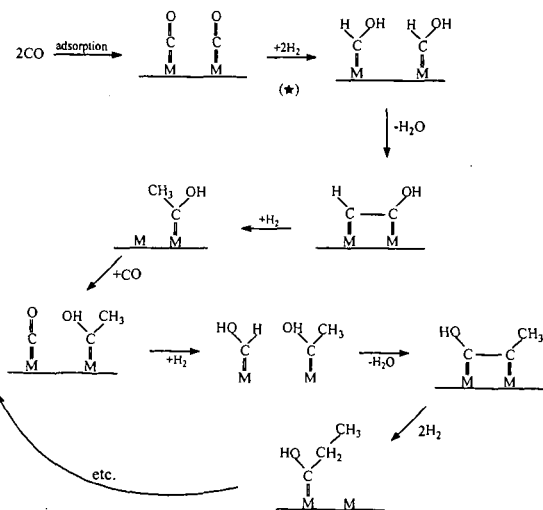
INTRODUCTION

The original **carbide mechanism** for the formation of hydrocarbon and oxygenate products with the Fischer-Tropsch synthesis (FTS) included the formation of the metal carbide followed by hydrogenation of the metal carbide to produce the products [1]. It was eventually recognized that this mechanism was inconsistent with thermodynamic data for the formation of hydrocarbons by hydrogenation of the carbide at the temperatures used for the synthesis reaction [2,3]. The direct hydrogenation of the metal carbide was investigated by Kummer et al. [4]. These workers performed iron carbide by the reaction of a reduced iron catalyst and ^{14}CO . The fraction of methane that is $^{14}\text{CH}_4$ when synthesis is effected with unlabeled CO is a measure of the contribution of direct hydrogenation of the preformed iron carbide to the synthesis. The data showed that carbide hydrogenation could be responsible for no more than 8 to 30% of the methane that is formed. These authors made a special effort to obtain data at low conversion levels that would represent the hydrogenation of only a percent of the total surface carbon; even under these conditions direct hydrogenation was responsible for only a small fraction of the methane produced. In addition, the same conclusion applied for the higher carbon number compounds. This study led most investigators to abandon the formation of a bulk metal carbide as an intermediate in the FTS mechanism.

About 1950, the **oxygenate (enol) mechanism** gained widespread acceptance [5,6]. This mechanism involves the chemisorption of CO which reacts with adsorbed hydrogen to form a species such as:



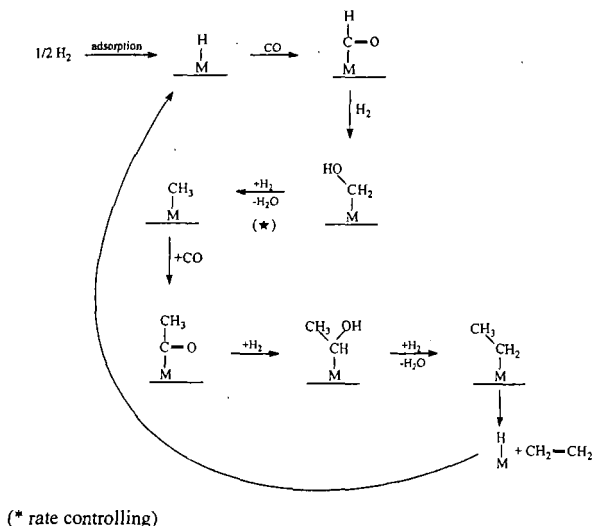
This structure grows by a combination of condensation and water elimination steps using adjacent groups. This enol group can condense as depicted in Scheme I below [7].



Scheme I

The results obtained by Emmett and coworkers [2,8-12] for their ^{14}C -tracer studies provided strong support for this mechanism. In these studies, ^{14}C -labeled alcohol or alkene was added together with the synthesis gas and the distribution of the isotopically labeled products was determined. It was found that the added alkene or the alcohol was able to serve to initiate chain growth. Much of the work by Emmett and coworkers was conducted at atmospheric pressure. However, our later work [13] using medium pressure synthesis and slurry phase reaction conditions produced results that were in agreement with the conclusions of Emmett and coworkers. In addition, our work showed that ethanol was incorporated 50 to 100 times as rapidly as ethene when the two reactants were converted under the same reaction conditions [14].

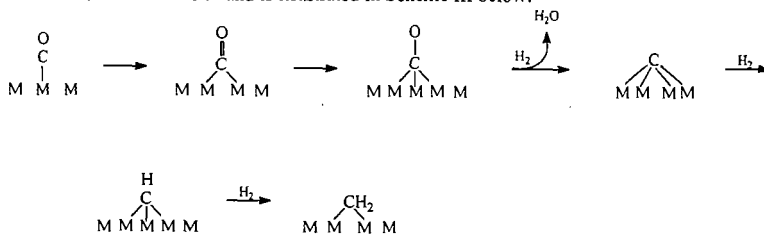
An **insertion mechanism** involves the insertion of CO into a metal-methyl or metal-methylene carbon bond which is then hydrogenated to produce an alcohol or alkene; the alcohol or alcohol precursor can also eliminate oxygen to produce an alkene product. One form of this mechanism is shown in Scheme II below [7,15]:



Scheme II

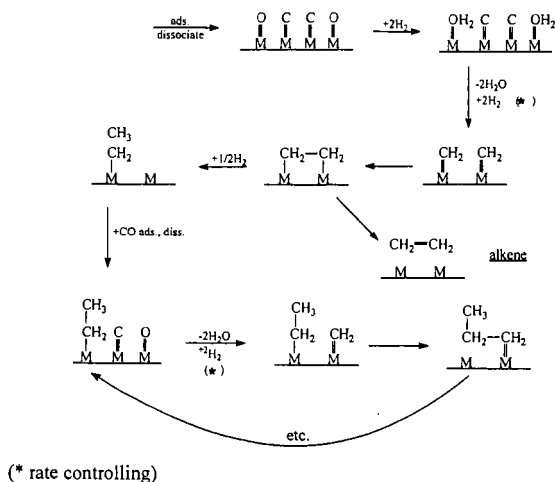
Hydrogenation and water elimination of the COH_2^* surface species are assumed to be the rate controlling step.

With the general availability of surface science instruments, it was found that CO adsorbs on single crystal metal surfaces to produce a surface covered with carbon, and little oxygen. This led to the conclusion that the CO chemisorbs and dissociates to adsorbed C and O. This step is followed by the rapid hydrogenation of adsorbed O to produce water. The hydrogenation of adsorbed carbon to form CH_2 is much slower. This mechanism may be viewed as a revival of the carbide theory but with the requirement that carbide formation is limited to the surface, or near surface, layer. Maitlis [16] has advanced this mechanism as the Fischer-Tropsch-Brady-Pettit-Biloen-Sachtler Mechanism and is illustrated in Scheme III below:



Scheme III

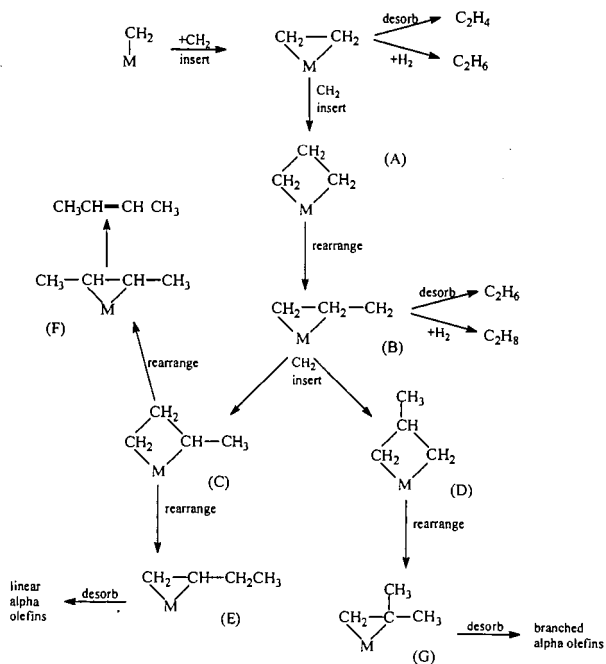
A more elaborate version of this mechanism has been provided by Dry and is shown in Scheme IV:



Scheme IV

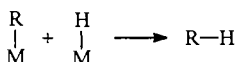
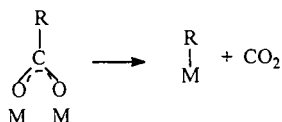
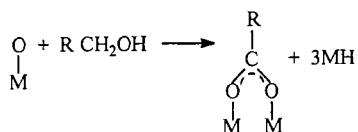
Dry considers the step(s) involving the hydrogenation of surface C to be rate-limiting; the other reactions are assumed to be at equilibrium.

A current view of the **carbide (carbene) theory** is illustrated in Scheme V [7]:

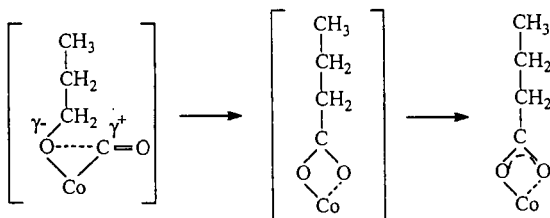
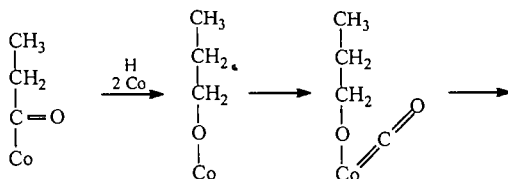
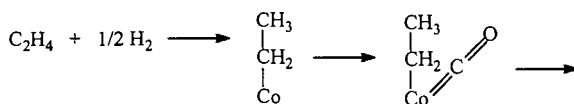


Scheme V

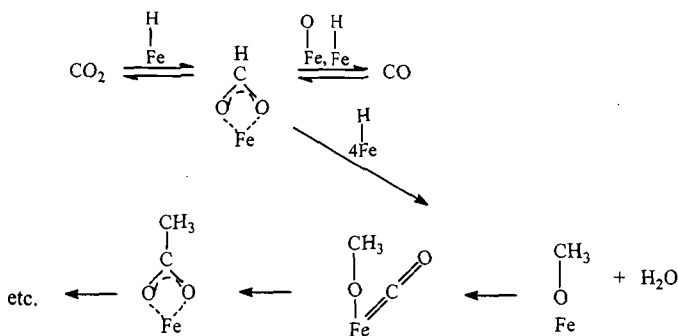
In the following we consider characterization data and try to combine this with results from isotopic tracer studies in an attempt to provide a mechanism that more nearly applies under conditions amenable to industrial practice. The consideration will be limited to the lower severity conditions likely to be encountered in slurry phase synthesis with an iron catalyst.



The conversion of ^{14}C labeled alcohols is consistent with the following reaction pathway: This reaction pathway allows for the direct formation of CO_2 and an alkane with one less carbon than the added alcohol, and is in agreement with the experimental results. Furthermore, there is valid infrared data to support the type of structure as being formed on metal (Fe and Co) surfaces. Thus, Blyholder et al. [17] offers the following mechanism for the reaction of CO , H_2 and C_2H_4 :



A similar adsorption model has been proposed by Kölbel and Tillmetz [18]. A pathway similar to the above would account for the chain initiation by CO_2 :



The oxygenate mechanism is able to account for the initiation by CO_2 as well as requiring chain propagation to occur only by CO since it appears unreasonable to expect CO_2 to be adsorbed with the structure shown in the Blyholder model.

In summary, there is clearly evidence for the participation of an oxygenate intermediate in the Fischer-Tropsch synthesis using an iron catalyst. It is also clear that a carbide is the more active form of the iron catalyst. The intermediate leading to the 1-alkenes remains to be identified.

On the other hand, the tracer studies with a cobalt catalyst are in agreement with a mechanism involving the carbene intermediate. Both CO_2 and alcohols behave as inert gases for the cobalt catalyst.

The next step is to provide more conclusive data to show that the mechanism for the iron and cobalt catalysts are indeed different. If, as the data suggest, they are different then the objective is to define the catalyst properties responsible for the difference.

ACKNOWLEDGMENT

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recovery technology continues to improve, one should expect that this price range will continue into the foreseeable future. However, this same history shows that the margin gap between gasoline prices and crude oil costs has been collapsing for the oil refining industry. Therefore, if crude oil prices continue to stay near \$20 per barrel, and the refining margins and gasoline prices continue to decline, it will be economically difficult to justify developing alternative fuel substitutes for gasoline and diesel.

Chart 5 shows the whole sale prices of a number of possible alternative fuels (on a energy equivalent basis) compared to conventional gasoline [4]. Only CNG (compressed natural gas) and LPG (liquid petroleum gas) appear to have some economic advantage relative to gasoline while ethanol, methanol and electricity are at a severe economic disadvantage. However, even these simple economics do not capture the added cost necessary to build the supporting fuel distribution infrastructure as well as the added cost of the vehicle to use that alternative fuel. These added costs will usually eliminate most if not all of CNG's and LPG's economic advantage over gasoline and further disadvantages the other alternative fuels. These unfavorable economics help explain the very small market share of AFVs that has developed since the crude oil price spike of the early 1980's. As shown in Chart 6, all the AFV fleets combined represent less than a quarter percent of the total U.S. vehicle fleet, and even these AFVs are usually found in niche markets that are supported by central fueling locations and favorable tax supports[5].

The economics do not appear to support the switch to alternative fuels and may not in the foreseeable future if crude prices stay near \$20 dollars a barrel. Therefore, AFV supporters have been using non-economic arguments such as using AFVs to reduce mobile source emissions from the vehicle fleet. Air quality agencies have been reducing tailpipe emission standards which provides an incentive to switch to AFVs with their lower emissions. In response, the oil and auto industries combined have found ways to further clean up gasoline and diesel fuels which not only reduces the emissions from the current vehicle fleet, but also allows the automakers to develop even cleaner burning vehicles that approach the lower emissions of the AFVs. Chart 7 shows the estimated emission reductions using the typical California Reformulated Gasoline in the current fleet relative to using 1990 industry average gasoline. As a result of the cleaner burning gasoline, the auto industry is now introducing cars that not only meet California's ULEV (ultra low emission vehicle) standard but also the SULEV (super ultra low emission vehicle) standard without using AFVs [7-11]. As new model gasoline vehicles becomes cleaner, the shrinking emission advantage of the AFVs diminishes to a point where the cost of reducing this small remaining emission becomes very costly compared to other options for reducing emissions elsewhere.

The most recent social quest has been to reduce the production of greenhouse emissions (mainly CO₂). To decrease mobile sources of these gases, the drive has been to reduce vehicle fuel consumption by moving to a higher efficiency vehicle with a fuel economy of 80 miles per gallon or 3 liters per 100 kilometers. To achieve this goal, many have thought it would require using a higher efficiency power train such as a fuel cell running on an alternative fuel such as hydrogen or methanol. However, the old workhorse combustion engine again appears to be rising to the challenge with the development of the high efficiency diesel engines coupled with hybrid drive trains [8,9,12-17]. Although the responsiveness and performance of the diesel engine has been improved to be comparable to that of the gasoline engine, a major hurdle still exists for reducing the diesel's NO_x (nitrogen oxides) and PM (particular) emissions to be comparable to gasoline engines. To help reduce these emissions, the reformulation of diesel continues to be studied. An example of recent work is shown in Chart 8 which shows that increasing the hydrogen content of the fuel will help reduce PM emissions by as much as 30 %. In addition, adding as much as 5 % oxygen can reduce emissions by another 25%[6]. With some success, the exhaust after-treatment technology for reducing emissions further may be able to decrease diesel tailpipe emissions enough to be comparable to that of gasoline [9,12-14,16].

CONCLUSIONS

When one looks at the recent history and current events, it suggests that the fuels of the foreseeable future will still be gasoline and diesel, but be improved, cleaner burning versions. These cleaner fuels will allow automakers to further develop even cleaner vehicles that will produce minimal emissions and consume much less fuel. Major improvements in the diesel engine performance and cleanliness will likely create a shift in the light duty vehicle market toward the higher efficiency and more economical diesel engine vehicle that seems to be occurring already in Europe. Future crude oil supplies always seem to be more plentiful than estimated in the past, and the technology and economic hurdles to convert other alternative energy sources into diesel and gasoline-like fuels also continues to improve. As a result of all these improvements combined, the economic incentives to switch to AFVs will not likely exist in the foreseeable future except for niche markets.

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Chart 1

Non-OPEC Oil Production Forecasts for 1987-89

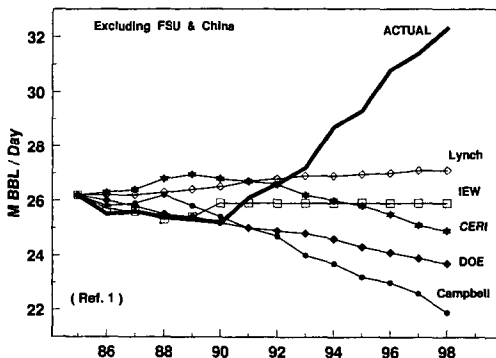


Chart 2

1987-89 Crude Oil Price Forecast

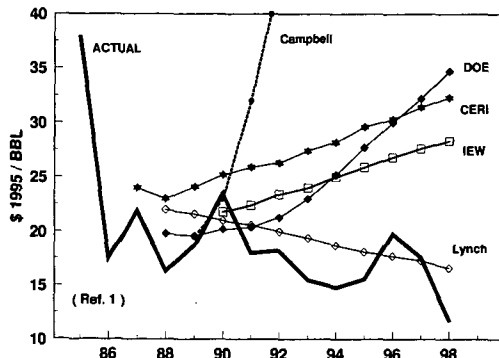


Chart 3

World Oil Consumption vs Oil & Gas Resources

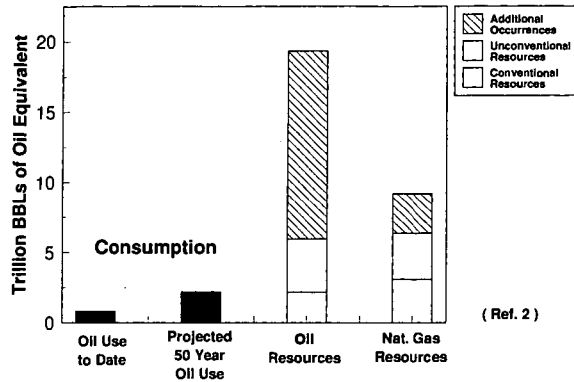


Chart 4

U.S. Crude Oil & Gasoline Price History

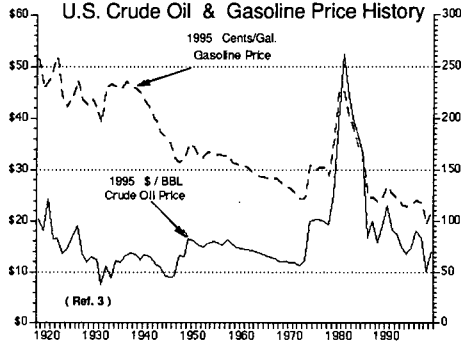
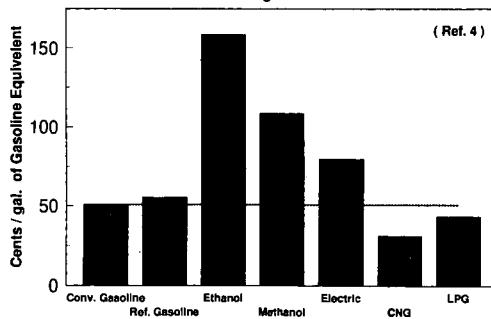


Chart 5

Economics Of Gasoline Alternative Fuels

1995 Wholesale Cost Before Adding Market Infrastructure & Vehicle Costs



Source: Alternative Transportation Fuels: A Comparative Analysis, AICHE Government Relations Committee, Sept 1997

Chart 6

1999 U.S. Vehicle Fleet: Alt. Fuel Vehicles vs Total Fleet

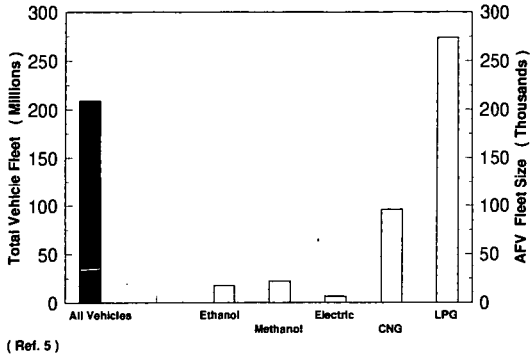


Chart 7

Emission Reductions with Calif. Reformulated Gasoline

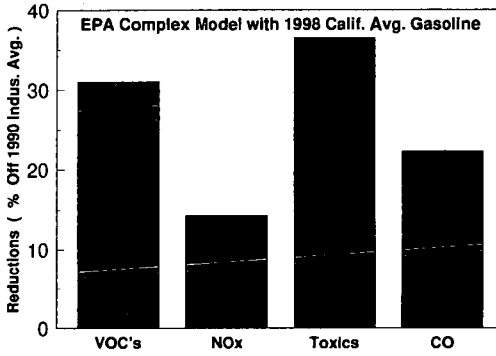
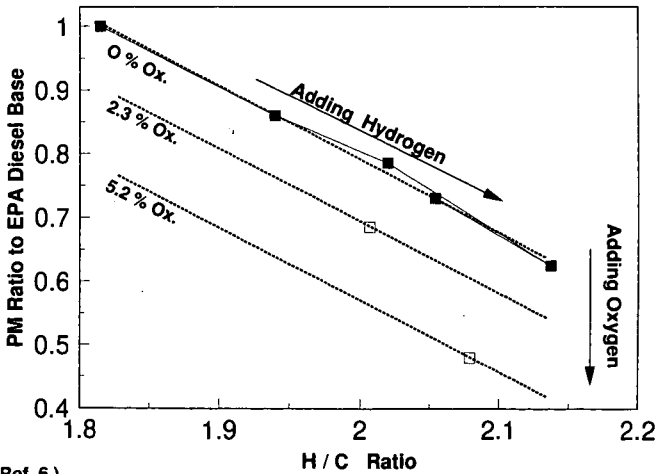


Chart 8

Adding Hydrogen & Oxygen Reduces Diesel PM



Fuels of the Future?

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Keywords: Crude Oil, Alternative Fuels, Diesel

INTRODUCTION

Since the first Oil Embargo, many in governments, industry and academia have been operating on the belief that alternative transportation fuels (and vehicles) will need to be developed to meet society's future mobile transportation requirements. The reasons for their beliefs varied over time from projected future high crude oil prices (economics), energy security, reducing mobile source pollutants and more recently, green house gases. As energy prices stabilized or declined, the economic and security arguments have diminished. An example of using AFVs (alternative fuel vehicles) for reducing mobile source pollutants was the U.S. Administration's original proposal in the 1990 Clean Air Act Amendments that would require the use of methanol fueled vehicles in the ten highest polluted cities. That policy proposal was eventually replaced by the Reformulated Gasoline (RFG) program. California made a similar attempt with their M85 (methanol) fuel program that has since seemed to stagnate.

In more recent years, California ratcheted down the tailpipe emission standards which pressured automakers to consider AFVs. However, the automakers found that they could take advantage of the cleaner burning properties of the reformulated gasoline to develop vehicles that could meet the tighter standards without investing in the more expensive AFVs. The most recent argument for AFVs has been to reduce green house gases. In response, the auto industry appears to be developing combustion engine technologies that may achieve the high fuel economy goals without switching to AFVs. Therefore, it appears that in the future the marketplace will more likely be converting the alternative energy sources into synthetic liquid fuels that look like gasoline or diesel instead of converting the vehicles to run on alternative fuels. Pursuing this pathway avoids much of the infrastructure economic hurdles that has burdened the development of the AFV market.

Does society or the marketplace need to switch to alternative fuels for future mobile transportation? Past and recent experience suggests that as gasoline and diesel quality becomes cleaner, the automakers are finding that they can burn these conventional fuels in vehicles more efficiently and cleanly by improving both the combustion engines and exhaust after-treatment technologies. This dampens, if not eliminates, the need for society to change over to an entirely new power train technology such as fuel cells. Therefore, it is highly likely that the fuel of the future will be a very clean gasoline or diesel. What is probably a more appropriate question is what will be the future hydrocarbon energy source for making gasoline and diesel in the future (natural gas or biomass?) as crude oil resources are eventually depleted. The following discussion reviews some of the issues that has driven the need (or belief) to switch to Alternative Fuel Vehicles (AFV).

DISCUSSION

The Oil Embargoes of the 1970's created a fear that oil supplies were declining and therefore helped spur the creation of the U.S. Department of Energy and the original push to develop fuel alternatives for gasoline derived from crude oil. Even though crude oil and energy is a commodity product, energy forecasters in the 1980's projected that crude supply alternatives to OPEC controlled crude would not develop (Chart 1)[1]. As a result, they ignored doing the fundamental cost analysis of the marketplace's ability to develop alternative crude supplies, and therefore projected that crude oil prices would climb much higher than \$20 per barrel (Chart 2)[1].

A common flaw in projecting a tightening crude supply market is to compare future oil consumption to the present estimate for conventional crude oil reserves, and thereby ignore the much larger supply of other oil resources and additional occurrences. The flaw in this economic supply demand analysis is the implicit assumption that oil recovery technology will not substantially improve to tap into these other potential oil supplies. When projected consumption is actually stacked against all oil sources, Chart 3 suggests that there may be a century worth or more of oil supply available for future oil markets [2]. Chart 4 shows that historical crude prices (corrected to a 1995 dollar basis) lie mostly between \$10 and \$20 per barrel [3]. Assuming oil